30741

Recon Stock

OTS: 60-31,637

JPRS: 3659

3 August 1960

INVESTIGATION OF THE VAPOR PHASE NITRATION OF CYCLOPENTANE HYDRO-CARBONS. III. NITRATION OF PROPYLCYLCOPENTANE

-USSR-

by M. A. Peredreyeva, Ya. I. Denisenko and S. S. Novikov

Distributed by:

OFFICE OF TECHNICAL SERVICES
U. S. DEPARTMENT OF COMMERCE
WASHINGTON 25, D. C.
~~Price: $0.50~~

U. S. JOINT PUBLICATIONS RESEARCH SERVICE
205 EAST 42nd STREET, SUITE 300
NEW YORK 17, N. Y.

JPRS: 3659

CSO: 4159-D

INVESTIGATION OF THE VAPOR PHASE NITRATION OF CYCLOPENTANE HYDRO-CARBONS. III. NITRATION OF PROPYLCYLCOPENTANE

-USSR-

[Following is a translation of an article by M. A. Peredreyeva, Ya. I. Denisenko and S. S. Novikov, Artillery Engineering Academy imnei F. Z. Dzerzhinskiy, in the Russian-language periodical Izvestiya Vysshykh Uchebnykh Zavedeniy SSSR-Khimiya i Khimicheskaya Tekhnologiya (News of Higher Educational Establishments of the USSR - Chemistry and Chemical Engineering), Ivanovo, Vol. III, No. 2, 1960, pages 312-315.]

The present work is a continuation of our research in the field of vapor phase nitration of cyclopentane homologues. In a previous work [1] we studied the nitration of methyl-cyclopentane and ethylcyclopentane. In this report the results of the vapor phase nitration of propylcyclopentane are presented.

EXPERIMENTAL PART

The propylcyclopentane, synethesized by us and subjected to nitration, had the following constants: b. pt. 130° C (746.3 mm); d^{20}_4 0.7758; n^{20}_D 1.4262; MR_D = 36.98. Calculated for C_8H_{16}: MR_D = 36.94. According to the data in the literature [2], b. pt. 129.5° (754 mm); $d^{20.2}_4$ 0.7772; n^{20}_D 1.4266.

Propylcyclopentane was nitrated with concentrated nitric acid (68%) at 340-400° C. The nitration process, study of the reaction products composition, separation and calculation of the yield of the nitro compounds were described in the previous work [1]. During the nitration of propylcyclopentane the dependence of the yield of the obtained nitro compounds on the reaction temperature was explained, in addition to the relationships of the hydrocarbons and nitric acid and the contact time of the reacting substances. The results and conditions of the experiments conducted are presented in Table 1.

TABLE 1

Dependence of the Yield of Nitro Products on the Reaction Temperature; Relationships of the Reagents and Contact Times

Taken for the reaction, moles		Reaction temp. °C	Molar ratio of hydrocarbon to nitric acid	Time of contact, sec.	Quantity of hydrocarbon, entering reaction, moles	Obtained Nitro compounds		Conversion of HNO_3, %
$C_5H_9C_3H_7$	HNO_3					Moles	%	
0.397	0.162	340	2.45	1.32	0.0313	0.0084	26.90	5
0.415	0.200	360	2.08	1.18	0.0436	0.0185	42.09	9
0.969	0.457	380	2.12	1.28	0.1321	0.1000	75.70	21
0.920	0.324	385	2.84	1.20	0.0944	0.0671	71.08	20
1.098	0.346	385	3.17	1.11	0.0892	0.0626	70.18	18
4.121	1.942	385	2.12	1.27	0.5598	0.4271	76.29	21
0.429	0.173	385	2.48	1.23	0.0525	0.0400	76.19	23
2.999	1.090	385	2.11	1.43	0.3152	0.2336	74.11	21
0.375	0.129	385	2.91	1.48	0.0384	0.0271	70.57	21
4.143	1.829	390	2.27	1.22	0.5509	0.4167	75.88	22
0.406	0.173	400	2.31	1.18	0.0545	0.0355	65.14	20
1.554	0.847	400	1.83	1.32	0.2679	0.1393	51.50	16

From these data it can be seen that at a 2.1-2.5 molar vatio of propylcyclopentane to nitric acid and 1.2-1.3 second contact time at an increased reaction temperature, the maximum yield of nitro compounds gradually increases reaching a maximum at 385°C. With a further increase in temperature at the given vatio of reagents and contact time, the yield of nitro compounds decreases due to pyrolysis of the formed nitro compounds.

Further, it can be seen that at the optimum temperature of 385°C and time of contact of about 1.2 seconds, the maximum yield of nitro compounds is obtained at a molar vatio of 2.1-2.5 of propylcyclopentane to nitric acid. At 385° and the vatio of reagents at 2.5, the optimal contact time of the reacting components is around 1.2-1.3 seconds.

Thus, it was established that the optimum conditions for obtaining the greatest yield of nitro compounds are: 385°C reaction temperature, a molar vatio around 2.5 of propylcyclopentane to nitric acid and 1.2-1.3 second contact time. Under these conditions the entire yield of nitro compounds, calculated on the hydrocarbon entering the reaction, reached 76%.

During the nitration of propylcyclopentane in the vapor phase, the chief products of the reaction are tertiary and secondary nitro compounds. From the data presented in Table 2, it is seen that considerably more secondary nitro compound is obtained than tertiary. So at the optimum reaction temperature of nitration (385°) more secondary nitropropylcyclopentane is obtained than tertiary, almost 40 times more. In addition, at low temperatures the ratio of secondary nitro product to the tertiary is less than at high temperatures.

TABLE 2

Ratio of Secondary and Tertiary Nitro Products

Reaction Temp. °C	Quantity of Nitro product, g.			Ratio of secondary to tertiary
	General	Sect.	Tert.	
360	26.04	24.05	1.19	12.09
380	15.80	15.21	0.59	25.78
385	125.07	122.01	3.06	39.89
385	132.60	129.39	3.21	40.45
390	27.38	26.73	0.65	41.12
400	14.47	14.15	0.32	44.21

The prepared tertiary nitro compound had the following constants: b. pt. 98° (10 mm); d^{20}_4 1.0031; n^{20}_D 1.4554; MR_D 42.49. Calculated MR_D 42.53. Found %: C 61.04; 61.23; H 9.61; 9.59; N 8.91; 8.83; $C_8H_{15}NO_2$. Calculated % C 61.15; H 9.55; N 8.92.

Judging from the physical constants, the chemical properties and the data from elementary analysis it can be considered that the tertiary nitro compound obtained by us is pure 1-nitro-1-propylcyclopentane. Tertiary nitro compound is a colorless oily liquid with a characteristic weakly camphor-like odor, readily soluble in alcohol, ether, hydro-carbons and other organic solvents. It is insoluble in alkalis and does not react with nitrous acid.

The secondary nitro compound had the following physical constants: b.pt. 103° (12 mm); 131° (40 mm); d^{20}_4 1.0019; n_D^{20} 1.4562; MR_D 42.60; Calculated MR_D 42.53.

Found %: C 61.20; 61.07; H 9.64; 9.58; N 9.03; 8.90. $C_8H_{15}NO_2$. Calculated %: C 61.15; H 9.55; N 8.92.

The secondary nitro compound, freshly distilled in a vacuum, is a colorless oily liquid, slowly yellowing upon standing in the light, possessing a characteristic odor resembling the odor of nitroparaffins; readily soluble in those same solvents as the tertiary product. It is readily soluble in concentrated aqueous alkali solutions; it reacts with nitrous acid in a clear-colored reaction which is characteristic for secondary nitro compounds.

A ketone was obtained by the oxidation of secondary nitro propylcyclopentane by an aqueous solution of potassium permanganate in an alkaline medium (3): the ketone had the following physical constants: b. pt. 67° (8 mm); d^{7}_7 0.9114; d^{20}_4 0.9006; n^{7}_D 1.4476; n^{20}_D 1.4434; MR_D 37.10. Calculated MR_D 36.96. According to the literature data (4), 1-propylcyclopentanone-2 has b. pt. 67° (8 mm); d^{7}_7 0.9111; n^{7}_D 1.4470.

The semicarbazone of the obtained ketone after recrystallization from methyl alcohol had the constant m. pt. 213°. In the literature (4) a m. pt. of 212-213° is given for the semicarbazone of 1-propylcyclopentanone-2.

Found %: N 22.92; 22.85; $C_9H_{17}ON_3$. Calculated %: N 22.95.

Thus the obtained secondary nitro compound appears to be 2-nitro-1-propylcyclopentane.

Amines were obtained by the reduction of the nitro compounds.

1-Amino-1-propylcyclopentane, obtained during the reduction of 1-nitro-1-propylcyclopentane by tin and hydrochloric acid, had b. pt. 165° (755.8 mm); d^{20}_4 0.8472; n^{20}_D 1.4510; MR_D 40.35. Calculated MR_D 40.55.

Found %: C 75.63; 75.50; H 13.31; 13.26; N 10.95; 11.06. $C_8H_{15}NH_2$. Calculated %: C 75.59; H 13.39; N 11.02.

The hydrochloride of 1-amino-1-propylcyclopentane, obtained during the action of hydrochloric acid on the amine, after recrystallization from hot water was a white crystalline substance, m. pt. 309° (with decomposition).

2-Amino-1-propylcylcopentane, obtained by reducing 2-amino-1-propylcyclopentane, had the following constants: b. pt. 172° (764.2 mm); d^{20}_4 0.8443; n^{20}_D 1.4518; MR_D 40.57. Calculated MR_D 40.55.

Found %: C 75.51; 75.62; H 13.36; 13.45; N 11.01; 11.09. $C_8H_{15}NH_2$. Calculated %: C 75.59; H 13.39; N 11.02.

The obtained amines, 1-amino-1-propylcyclopentane and 2-amino-1-propylcyclopentane, are colorless, mobile liquids, distillable without decomposition at the usual pressure, having a sharp ammonia odor, poorly soluble in water; aqueous solutions give an intensive violet color with the addition of phenolphthalein. They are readily soluble in ether, benzene, acetone and other organic solvents. With carbon dioxide they yield the highly volatile carbonates - white crystalline substances.

The hydrochloride salt of 2-amino-1-propylcyclopentane, obtained in an atmosphere of dry hydrogen chloride, is a white crystalline substance, deliquescent in air and in dry hydrogen chloride: m. pt. 78°.

The chloroplatinate of 2-amino-1-propylcyclopentane is a yellow crystalline substance. Found %: Pt 29.31; Calculated %: Pt 29.39.

RESULTS

1. The nitration reaction of propylcyclopentane by concentrated nitric acid in the vapor phase was studied. It was established that during the vapor phase nitration of propylcyclopentane the secondary nitro product chiefly is obtained - the 2-nitro-1-propylcyclopentane and a small quantity of the tertiary nitro compound - 1-nitro-1-propylcyclopentane.

2. The effect of the reaction temperature, the ratio of reagents, the contact time and other factors affecting the yield of the nitro compounds were clarified.

There was shown that the optimal conditions for obtaining the greatest yield of nitro compounds are: reaction temperature of 385°C, molar ratio of propylcyclopentane to nitric acid of about 2.5 and a contact time of 1.2-1.3 seconds. Under these conditions the entire yield of nitro compounds reached 76%.

References

1. Denisenko, Ya. I. and Peredreyeva, M. A., Izvestiya Vysshyka Uchebnykh Zavedeniy- Khimiya i Khimicheskaya Tekhnologiya (News of the Higher Educational Establishments - Chemistry and Chemical Engineering), 2, 720, (1959).

2. G. Chavanne, P. Becker, Bull Soc. Chim, Belgique, 36, 599, (1927).

3. Nametkin, S. S. and Pozdnyakova, Ye. I., Zhurnal Russkogo Khimicheskogo Obshchestva (Journal of the Russian Chemical Society), 45, 1420 (1913).

4. C. Vavon, J. Flurer, Bull Soc. Chim. France, (4) 45, 754 (1929).

Chair of Chemistry

Arrived at the editor's office: 11 July 1958

5551

-END-